OPTICAL CONSTANTS OF METALS IN THE EXTREME ULTRAVIOLET

II. ON THE OPTICAL CONSTANTS OF ALUMINUM, MAGNESIUM AND INDIUM AT WAVELENGTHS SHORTER THAN THEIR CRITICAL WAVELENGTHS*

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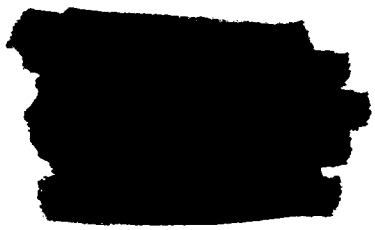
For publication in

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA

*Supported, in part, by National Aeronautics and Space Administration - Contract R-21

(7140-PRR-17/63:WRH:pj)



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ABSTRACT

Measurements of the index of refraction of Al, Mg and In as a function of wavelength have been made from 300 Å to their critical wavelengths. The measurements, made on films evaporated onto glass substrates, were obtained using a "critical angle" technique. It was found that the index of refraction of Al and Mg in this wavelength range can be described to a good approximation by the free electron theory of Drude, while that of In can not. The extinction coefficient was calculated for Al and Mg on the basis of the free electron theory and, in the case of Al, compared with measured values. The optical properties of Al over a wavelength range from 300 to 6000 Å are discussed and compared with results predicted by the free electron theory.

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* Supported, in part, by NASA Contract R-21.

I. INTRODUCTION

An explanation of the properties of metals in terms of free electrons existing in thermal equilibrium with the atoms of the solid was first given by Drude.[1] Despite its simplicity, the theory was successful in explaining a number of phenomena and even today is considered the cornerstone of the theory of metals.

In applying the theory to a description of the optical properties of metals, it is convenient to use it in the two parameter form shown below.

$$\epsilon_1 = n^2 - k^2 = 1 - \frac{\omega_c^2 \tau^2}{1 + \omega^2 \tau^2} \tag{1}$$

$$\epsilon_2 = 2nk = \frac{1}{\omega \tau} \frac{\omega_c^2 \tau^2}{1 + \omega^2 \tau^2} \tag{2}$$

In the limit as τ approaches infinity, Eq. (1) becomes,

$$\epsilon_1 = n^2 = 1 - \frac{\omega_c^2}{\omega^2} \tag{3}$$

and Eq. (2) becomes zero since k becomes zero.
ϵ_1 and ϵ_2 are the real and imaginary parts of the complex dielectric constant, respectively, and n is the index of refraction and k the extinction coefficient. The parameters are: τ, which is the relaxation time of the electrons,

caused by collisions with the atoms of the metal, and ω_c which is the critical frequency. A simple physical picture of ω_c may be obtained from Eq.(3). If the frequency is less than ω_c, the index will be imaginary, energy cannot propagate in the medium and there will be total reflection at all angles of incidence. On the other hand, if the frequency is greater than ω_c, the index is real but less than unity so energy will propagate in the medium although it can only enter the medium if the angle of incidence is less than the critical angle. Hence ω_c, or the critical wavelength λ_c, is the wavelength at which an ideal metal changes from a totally reflecting to a transmitting medium.

ω_c is also known as the plasma frequency, or valence electron collective oscillation frequency, and is the frequency at which the free electrons in the metal will oscillate collectively because of the coulomb interaction. The value of ω_c depends only on the electronic charge, mass and density in the solid, and is given by:

$$\omega_c^2 = \frac{4\pi Ne^2}{m} \tag{4}$$

where e is the charge on an electron, m the free electron mass and N the valence electron density.

R. W. Wood's[2] experiments on the optical properties of the alkali metals in the ultraviolet were the first to show the high transparency of these metals in the spectral region below their critical wavelengths. Zener's[3] explanation of the phenomena in terms of completely free electrons, although qualitatively correct, required total reflection at wavelengths longer than the critical wavelength which was not the case. Equation (3) describes Zener's theory. Subsequently, Kronig[4] showed that damping of the electron motion due to collisions with the lattice would explain the absence of total reflection and still retain a critical wavelength below which the transmittance would be large. Kronig's explanation was equivalent to the free electron theory of Drude and is represented by Eqs. (1) and (2) above.

It is to be expected that the alkali metals with their single valence electrons and tightly bound cores would follow the free electron theory. This was borne out by the work of Ives and Briggs[5] who measured the optical constants of the alkali metals in the visible and ultraviolet to 2536 Å. They found that the optical properties of sodium were described fairly accurately by the free electron theory but direct application of the theory to the other alkali metals was not as successful.

It might be expected that other metals classified as having loosely bound valence electrons and tightly bound cores will also follow the free electron theory, at least in some spectral regions. In a review article on collective energy losses in solids, Pines[6] has discussed the classification of metals by the binding energy of the valence and core electrons. Those with loosely bound valence electrons and tightly bound cores include Be, B, C, Al, Mg, Si and Ge. Hass, Hunter and Tousey[7,8] have observed the transparency of Al at 736 Å and 584 Å and succeeded in measuring an index of refraction and an extinction coefficient at those wavelengths. They found that n is increasing and k decreasing as the wavelength becomes shorter. Walker, Rustgi and Weissler[9] have measured the reflectance and transmittance of various evaporated metal films and found, in the case of Al, that the reflectance decreased as the wavelength increased to the critical wavelength and that beyond λ_c, the transmittance increased out to the shortest wavelength at which they could measure, thus confirming the decrease in k with λ observed by Hass, et al. Two of the seven substances mentioned above, Al and Mg, are included in this work and have been found to follow the free electron theory to a good approximation. The third,

In, is classified by Pines as having core electrons that are not truly tightly bound and it could not be described by the free electron theory.

II. EXPERIMENTAL PROCEDURE

Visually opaque films of metal on glass of thicknesses in excess of 1000 Å were produced by evaporation under optimum conditions as described by Hass, Hunter and Tousey.[10] Aluminum and indium of 99.999% purity were used; aluminum being evaporated from tungsten filaments and indium from a tungsten boat. Magnesium, of 99.98% purity, was evaporated by electron bombardment. All evaporations were rapid, opaque films being produced in 1-2 seconds and, except for magnesium, at pressures less than 10^{-5} torr. During the evaporation of the magnesium, the pressure was $3\text{-}5 \times 10^{-5}$ torr. A criterion for the quality of the aluminum mirrors was the reflectance at 1216 Å which was compared with previously reported measurements.[10] No such criteria were available for the other two metals and it was necessary to investigate the effects of evaporation conditions on the repeatability of the measurements.

Samples were transferred as rapidly as possible to the reflectometer where the reflectance was measured, and n was obtained by the critical angle technique discussed in the preceding paper. Angles were precise to $\pm 1/2^{o}$, which corresponds to an accuracy of about ± 0.01 in n. Measurements were commenced within 5 minutes of the evaporation and completed in about three hours, so that the oxide layer was less than 15 Å thick.[11]

III. RESULTS

The results for aluminum are shown in Fig. 1. In the upper half of the figure, the small dots through which the solid curve was passed show the values of n derived from the position of maximum slope. Values obtained from fringe spacing measurements discussed in the preceding paper, are plotted as large solid circles. The measured values of n agree with those obtained by LaVilla and Mendlowitz,[12] who calculated the complex dielectric constant from 1055 Å to 680 Å by means of the Kronig-Kramers dispersion relation using data obtained from inelastic scattering of electrons by thin foils. Their results, uncorrected for possible contributions by absorption processes at long and short wavelengths,

were converted to optical constants and plotted as crosses. The measured values of n are also in good agreement with values calculated using the Drude free electron theory, shown as open circles. In the calculation a critical wavelength of 837 Å and a relaxation time of 1.1×10^{-15} seconds,[12] were assumed. The index is not sensitive to the value chosen for τ, however, for wavelengths shorter than 700 Å.

In the lower half of the figure are plotted the calculated values of k obtained using the Drude theory with values of τ ranging from $0.4\text{-}1.2 \times 10^{-15}$ seconds. A value of 1.2×10^{-15} seconds was deduced by Mendlowitz[13] from measurements of optical constants in the near ultraviolet and visible regions by Hass and Waylonis.[14] The two large solid circles are experimental values of k, obtained by transmission measurements through unbacked films of different thicknesses.[8] They follow, approximately, the k curve corresponding to $\tau = 0.7 \times 10^{-15}$ seconds. Subsequent indirect determinations of k made by Madden, Canfield and Hass[15] from the shape of the reflectance versus angle of incidence curve at angles larger than α_c for unoxidized aluminum, gave substantially the same value of k. The k values obtained from the data of LaVilla and Mendlowitz which are shown as crosses indicate that τ should be even

larger than 1.2×10^{-6}. As the wavelength approaches 800 Å, the value of k increases and becomes large enough to effect the position of the angle of maximum slope, as discussed in the preceding paper. Values of k corresponding to $\tau = 0.7 \times 10^{-15}$ seconds were used to obtain the corrected curve, shown as the broken line in the upper half of the figure, because they fit the experimental data best.

Figure 2 compares the current optical properties of aluminum over the wavelength range from 300 Å to 6000 Å with those calculated from the free electron theory. The two solid curves represent n and k, calculated using the free electron theory, with $\lambda_c = 837$ Å and $\tau = 1.1 \times 10^{-15}$ sec. The broken curve is the reflectance at normal incidence calculated from these values of n and k. Values of n from 300 Å to 800 Å, obtained from the corrected index curve in Fig. 1 are shown here as open circles while the solid circles at 584 Å and 736 Å represent, as before, the results of fringe and transmission measurements. From these latter two sets of values the reflectance at 584 Å and 736 Å was calculated since the presence of interference effects in evaporated films on glass prevented measurements of the true normal-incidence reflectance below 800 Å. From 2200 Å to 6000 Å, plus signs show the measured values of

n,k and reflectance reported by Hass and Waylonis. The triangles from 1025 Å to 2000 Å are the reflectance values obtained by Madden, Canfield and Hass, while the crosses are the values calculated from the paper of LaVilla and Mendlowitz.

With a few exceptions, the agreement between measured and calculated values of the optical properties is excellent. From 3000 Å to longer wavelengths, the measured values depart, slightly, from the calculated values because of interband transitions occurring at approximately 8000 Å which are not included in the free electron theory. Madden, Canfield and Hass were unable to measure n and k from 2000 Å to 1000 Å because the rapid oxidation caused the reflectance to decrease during the time required to make a measurement. The reflectance values they reported were obtained by extrapolation to zero time, following the linear relation found by them to hold during the first 50 seconds after the evaporation. The values between 700 and 1055 Å, derived from the work of LaVilla and Mendlowitz, generally show very good agreement with both the values obtained by the critical angle technique and the calculated values. Errors in reading their data caused the large departure of n from the calculated values at 1055, 1028 and 987 Å, which, in turn, caused the

calculated reflectance to be higher than that calculated using the free electron theory. At wavelengths shorter than 800 A, their k values are smaller than the calculated values. This trend is not considered significant because, from Eq. (4), LaVilla and Mendlowitz have calculated that the effective number of valence electrons participating in the collective oscillation at 837 A is 2.6, hence, additional absorption must occur for $\lambda > \lambda_c$ to account for three valence electrons. The amount of additional absorption has been estimated at about 13% by Stern and McGroddy[16] who summed the interband oscillator strengths, using published data from the long wavelengths to 2000 A, 6 ev, and estimated values for n and k from 2000 to ω_c. Thus, it is expected that k will be larger than that calculated using the free electron theory at $\lambda > \lambda_c$. This is borne out by the two measured values of k at 584 A and 736 A.

A few investigators have reported values of n and k for aluminum between 1000 A and 2000 A. Cole and Oppenheimer[17] have measured values of n and k by the general reflectance

method at 1216 Å, 1048 Å, 920 Å, 584 Å and 304 Å. Their k values are in reasonably good agreement with the calculated curve at 1216, 1048 and 920 but their n values at these wavelengths are almost an order of magnitude larger than those calculated using the free electron theory. At 584 and 304 Å, their n values are in good agreement but their k values are much too high.

Schroeder[18] has also reported values of n and k between 1000 and 2000 Å, obtained by fitting a Cauchy dispersion formula to the data of Hass and Waylonis at $\lambda > \sim 2200$ Å and to the data at 1216 Å reported by Berning, Hass and Madden.[11] His results are similar to those of Cole and Oppenheimer in that the n values are an order of magnitude higher than the calculated values while the k values are in better agreement.

The true values of n and k from 1000 to 2000 remain to be determined. However, considering the data available, it is expected that the measured values will agree fairly well with the calculated values shown by the solid lines. A deviation may occur at approximately 1200 Å due to a surface plasma oscillation[19] and, in fact, the reflectance shows a slight dip at 1216 Å.

The results for magnesium are shown in Fig. 3. In the upper section the dots represent the index measurements, and the open circles calculations using the free electron theory with λ_c = 1198 Å and τ = 1.1 x 10^{-15} seconds.[20] A curve having the form outlined by the calculated values was drawn through the experimental points and shows that the index of Mg follows, approximately, the free electron theory although not as closely as in the case of Al. The data points from 600 Å to 800 Å show a greater departure from the smooth curve than the other points and is attributed to uncertainties in the measurements. However, some electron scattering experiments[21] show a broad peak centered at about 20 ev, believed to be due to MgO, which may have influenced the results

The lower part of the figure shows k, calculated using the free electron theory. Tomboulian and Kroger[22] have made photographic measurements of the transmittance versus wavelength of Mg films evaporated onto zapon, and found structure in the curve that they attributed to inter-band transitions. They calculated the index of refraction and μ, the absorption coefficient using more sophisticated theories and obtained structure in the μ versus wavelength curve corresponding roughly to that they observed. Their

calculated values of μ, converted to k, were of the same order of magnitude as k calculated using the free electron theory, however, their calculated values of n depart widely from the values shown in Fig. 5 at 800 Å and the wavelength dependence is quite different.

The k versus wavelength curve calculated from the free electron theory cannot be expected to show structure, of course, so if the inflection in the n curve between 600 and 800 Å is real, the k values may show a corresponding departure from the calculated curve at these wavelengths. It is expected, however, that this departure will not be large and that the curve shown is a fair approximation to reality. It has been used to correct the index curve, the correction being shown by the broken line in the upper half of the figure.

The index of refraction of indium is shown in Fig. 6. Data obtained from bright, shiny surfaces and from slightly hazy surfaces were in very good agreement, and the scatter of data points is less than for either of the other two metals. For wavelengths shorter than 800 Å, however, the region of α_c was indistinct and the points shown are uncertain. The extinction coefficient is still small from 800 to 744 Å because interference fringes were observed,

however, between 744 and 736 Å, the fringes disappeared and the metal became opaque. This is in agreement with the work of Walker, Rustgi and Weissler[9] who observed a sudden termination in transmittance of indium foils at 16.8 ev which they attributed to interband transitions.

No values of k have been reported for indium so that the index curve could not be corrected. Furthermore, the results do not fit calculations using the free electron theory for any value of τ.

ACKNOWLEDGMENTS

The author is indebted to R. Tousey and R. LaVilla for many helpful discussions.

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CAPTIONS

Figure 1 - Optical constants of aluminum from 300 Å to 800 Å. In the upper half of the figure the solid line is passed through the values of n derived from the angle of maximum slope (dots). The two large solid circles are values obtained from fringe positions; the crosses are values calculated from the paper of LaVilla and Mendlowitz; the broken curve is as corrected for the effect of $k \neq 0$. The open circles are calculations using a Drude-type model with λ_c = 837 Å and $\tau = 1.1 \times 10^{-15}$ sec. In the lower half of the figure the solid lines represent k, calculated using the same type model for different values of τ; the two large solid circles are values obtained from transmission measurements and the crosses are calculated from the data of LaVilla and Mendlowitz.

Figure 2 - Current status of the optical properties of aluminum from 300 Å to 6000 Å. The two solid curves represent the optical constants and the broken curve is the normal-incidence reflectance, calculated using a Drude-type model with λ_c = 837 Å and $\tau = 1.1 \times 10^{-15}$ seconds. The open circles are values taken from the corrected curve of Fig. 1; the solid circles represent data obtained from fringe positions and transmission measurements; the crosses are

calculated from the data of LaVilla and Mendlowitz; the triangles are reflectance data from Madden, Canfield and Hass and the plus signs are the data of Hass and Waylonis.

Figure 3 - Optical constants of magnesium from 300 Å to 800 Å. In the upper half of the figure the solid line is passed through the values of n derived from the angle of maximum slope (dots). The open circles are calculated using a Drude-type model with λ_c = 1198 A and $\tau = 1.1 \times 10^{-15}$ seconds. The broken curve is the correction for the effect of $k \neq 0$. In the lower half of the figure the solid line represents k calculated using the same parameters shown above.

Figure 4 - Index of refraction of indium from 800 to 1100 Å. The solid curve has been passed through the values of n derived from the angle of maximum slope (dots).

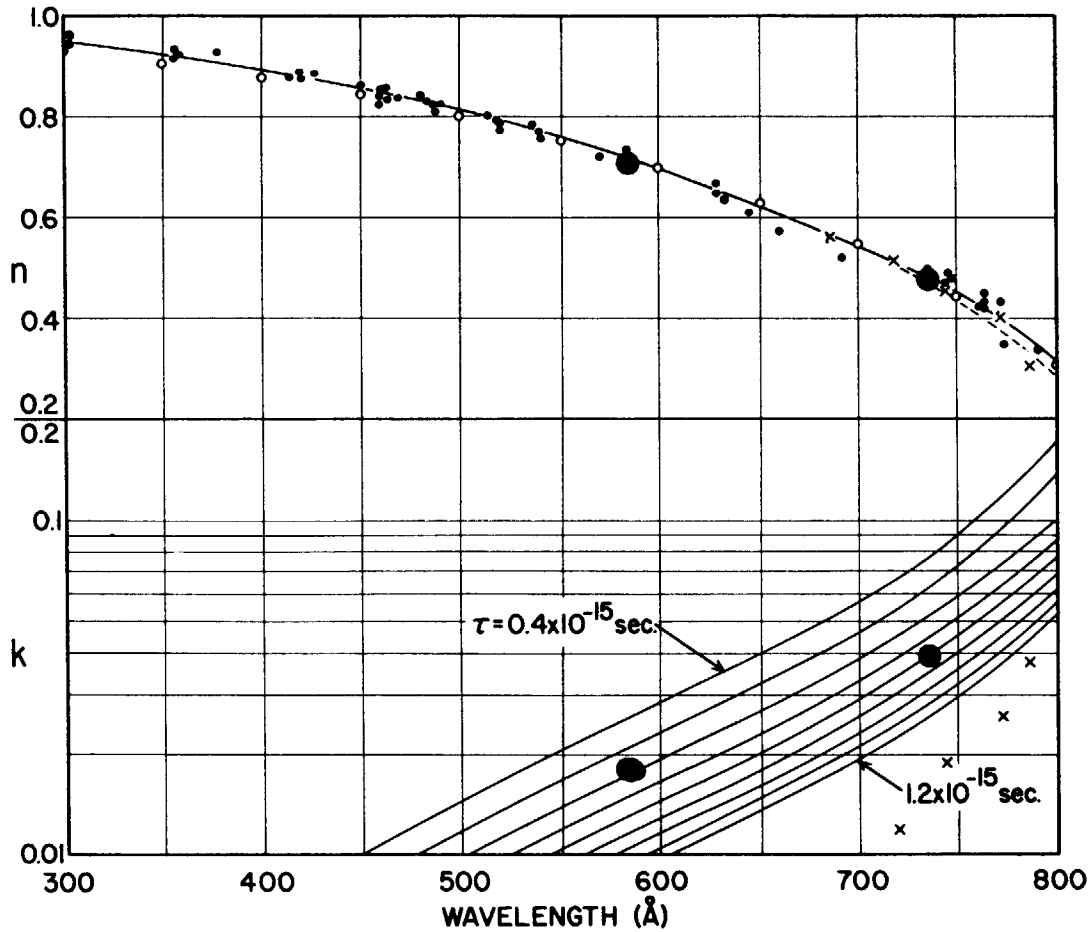
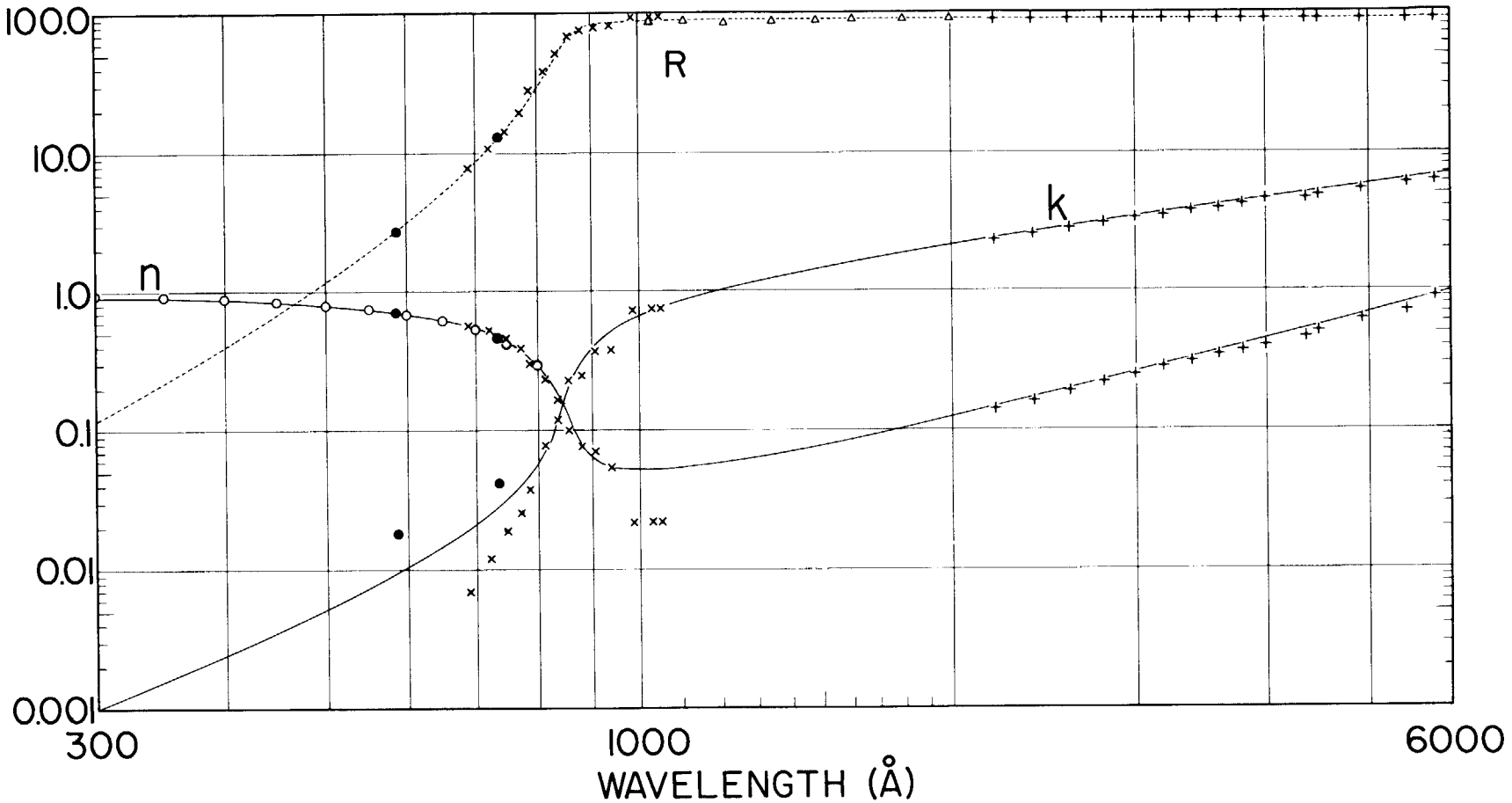


Figure 1

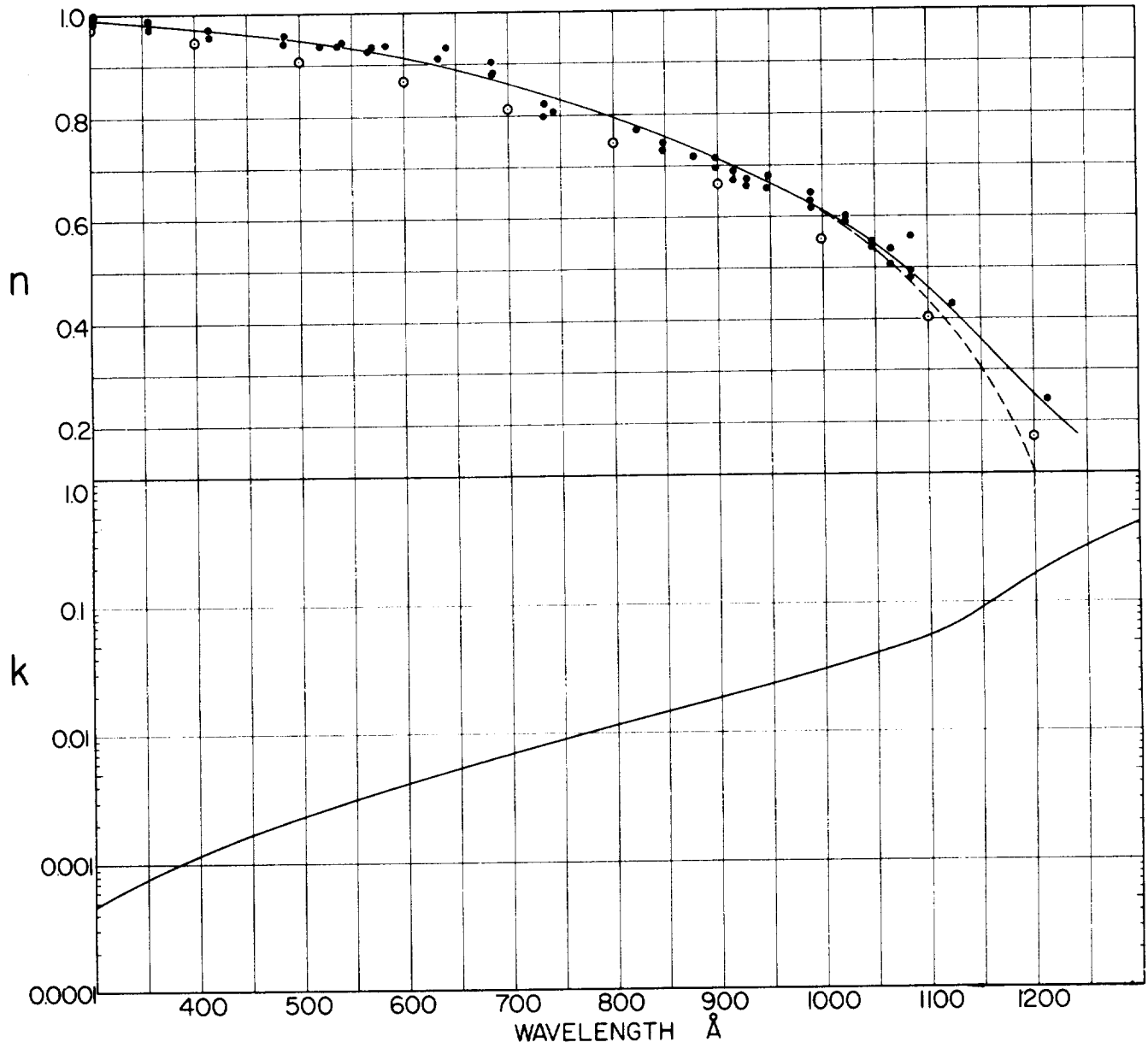
↓ INDEX OF REFRACTION OF ALUMINUM.

↓ EXTINCTION COEFFICIENT OF ALUMINUM CALCULATED FOR DIFFERENT VALUES OF THE RELAXATION TIME τ.



OPTICAL CONSTANTS & NORMAL INCIDENCE REFLECTANCE OF ALUMINUM

Figure 2



| INDEX OF REFRACTION OF MAGNESIUM

| EXTINCTION COEFFICIENT OF MAGNESIUM CALCULATED USING THE FREE ELECTRON THEORY. (λ_c=1198Å, τ=1.1x10^{-15}sec.)

Figure 3

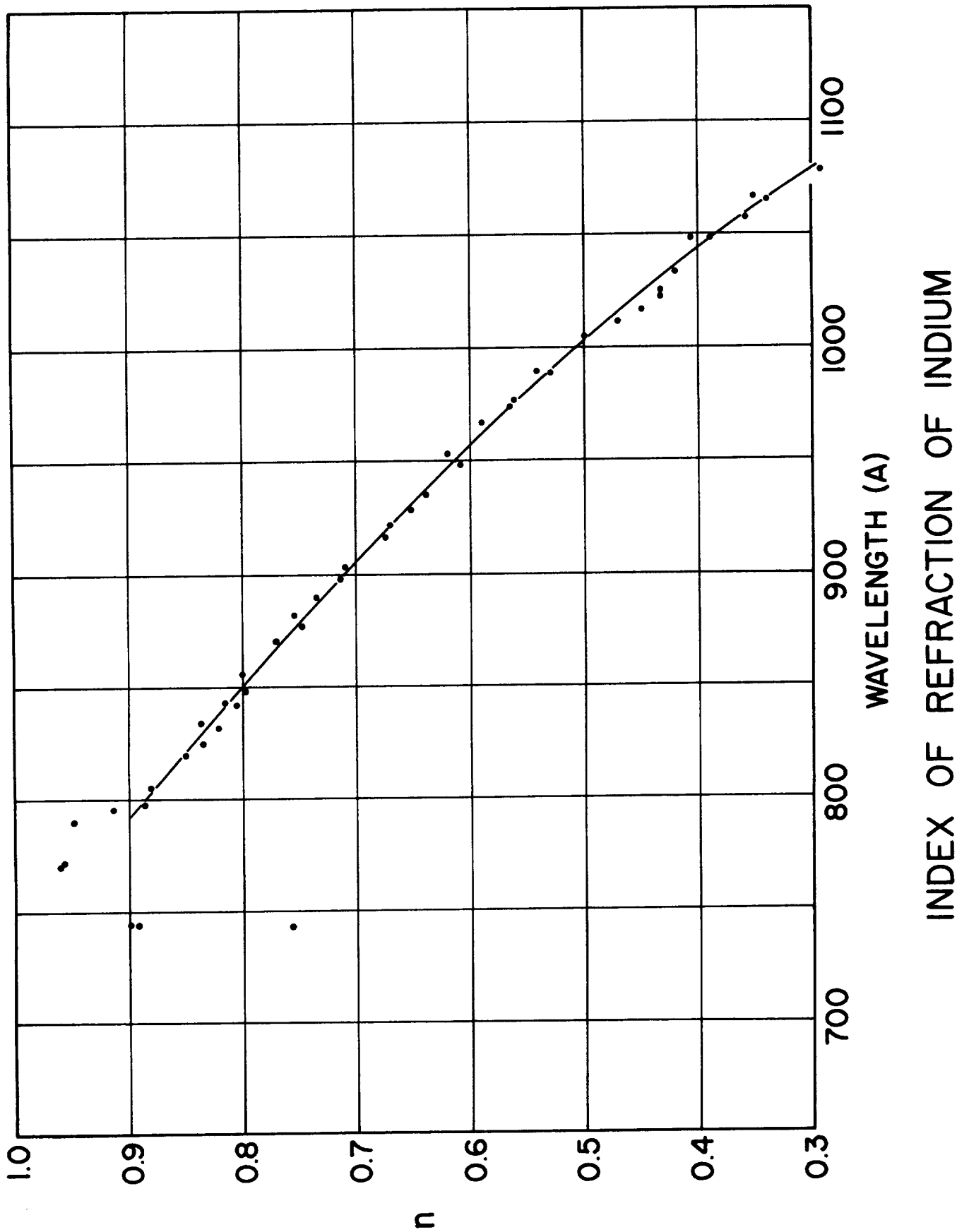

INDEX OF REFRACTION OF INDIUM
WAVELENGTH (A)
700
800
900
1000
1100
n
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 4